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Structure and Properties of Lightly Crosslinked Isotactic Polypropylene, Crystallized from the Melt Under Uniaxial Compression

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The structure and properties of lightly crosslinked isotactic polypropylene films prepared under conditions involving molecular orientation are studied. It is confirmed by small angle X-ray scattering and differential scanning calorimetry that samples crystallized from the melt under uniaxial compression have a highly ordered crystalline phase associated with high melting and shrinking temperatures.** The long period, scattering intensity and melting temperature increase in accordance with increasing degree of compression and a characteristic dual peak appears in the DSC fusion curve. Furthermore, studies of the dynamic mechanical relaxations of the samples reveal that the α_a transition temperature ascribable to mocro-Brownisn motion of molecular chains in the amorphous phase is not altered but the α_c transition temperature ascribable to some local motions in the crystalline region is shifted to a higher temperature with increasing degree of compression.

KEY WORDS: Isotactic polypropylene/ Uniaxial compression/ Small angle X-ray scattering/ Melt-compressed polypropylene/

I. INTRODUCTION

In a previous paper,[1] it is found that a particular planar orientation of crystal planes appears when a crosslinked isotactic polypropylene is crystallized from the melt under uniaxial compression. The orientation of crystal plane (040) perpendicular to the compression direction appears at relatively low degree of compression; at higher compression the (110) and (130) planar orientations follow. Such planar orientations are assumed to be associated with unique macroscopic properties of the samples.[2-5] This paper deals with the macroscopic properties such as mechanical, thermal properties in relation to the phase structures of the samples.

II. EXPERIMENTAL

1. Samples

A molecular weight fraction was obtained from a commercial isotactic polypropylene by liquid-liquid separation technique using xylene and a polyethylene glycol. The viscosity average molecular weight of the sample was determined to be 4.0×10^5 by viscosity measurements in decaline at 135°C. Here, viscosity average molecular weight was calcu-

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** Since lightly crosslinked sample exhibits rubbery elasticity in the melt, the crystallization under compression is carried out with holding the orientation of chain molecules.[1]

lated using the relation, $[\eta]=1.38\times10^{-4}\,M^{0.84}$, established by Kinsinger.[6]

Film sample made from this molecular weight fraction was crosslinked by irradiation with ^{60}Co γ-ray to 10 Mrad in an acethylene atmosphere at room temperature. For further studies this sample was used after extracting the soluble part (20%) with boiling xylene. The detailed procedure was reported in the previous paper.[1]

The gel sample in film form thus obtained was next uniaxially compressed to different degrees in the melt at 180°C between two metal plates and cooled to room temperature over a period of 15 min. For the purpose of comparison uncrosslinked original sample was also compressed at a temperature of 150°C below the melting point. The degree of compression was characterized by the ratio of film thicknesses before and after compression, designated as compression ratio. It ranged 1 to 15.

2. Density and Crystallinity

Densities of samples were measured at 30°C by a density gradient column composed of ethylene glycol and n-propylalcohol. The crystallinity was obtained from the measured density according to the relation;

$$\text{Crystallinity}=\frac{0.983+9(t+180)\times10^{-4}-1/d}{4.8(t+180)\times10^{-4}}$$

established by Natta[7] with the assumption of the additivities of the specific volumes of the crystalline and amorphous phases. Here, d and t designate the measured density and the ambient temperature in centigrade, respectively.

3. Small Angle X-ray Scattering (SAXS)

The SAXS patterns were obtained at room temperature with a point collimation Rigaku Denki small angle X-ray camera. This X-ray work was carried out with Ni-filtered Cu-Kα beam under vacuum with 50 kV, 80 mA, and 0.3 mm primary beam diameter and a specimen to film distance of 300 mm. SAXS scanning was carried out with a Kratky camera to obtain the long period.

It was evaluated from the scattering angle at the maximum in the scattering profile after subtracting the base line, using the Bragg's relation.

4. Fusion and Enthalpy Change in Fusion

The fusion curve was obtained by a differential scanning calorimetry with use of the Perkin Elmer DSC 1-B. The amount of the sample used was about 3–4 mg and the correction of temperature was made with use of pure Indium. The melting point was defined to be a temperature where the fusion finally terminated. The enthalpy change in the fusion was estimated by planimetry of the fusion curve with a reference datum for purified benzoic acid.

5. Dimensional Change with Temperature

The dimensional change with increasing temperature at a rate of 1°C/min in air was measured by a cathetometer under a constant load 1 g/mm^2.

6. Dynamic Mechanical Properties

The temperature dependence of the loss tangent than δ, the dynamic modulus E′ and dynamic loss E″ was measured by a type of forced vibrational method with the Vibron

DDV-2 (Toyo Baldwin Co.,). The selected frequency for the measurement was 110 cps and the values tan δ, E′ and E″ were obtained in a range of temperature from −30° to +140°C at a heating rate of 0.5°C/min. The dimension of the test pieces was 30 mm in length, 0.1–0.2 mm² in cross section.

III. RESULTS AND DISCUSSION

1. Small angle X-ray Scattering (SAXS)

SAXS patterns for the two series of samples; (A) compressed at 150°C in the partially crystalline state (hereafter designated "plastically compressed samples") and, (B) compressed at 180°C in the melt (hereafter designated "melt-compressed samples"), were first examined. When the X-ray beam was introduced perpendicular to the film surface of samples, diffuse patterns were obtained for all samples and the diffractive intensity was distributed circularly around the beam direction in the range of small angles. Those patterns implied a random uniaxial distribution of crystallites around the beam direction, namely around the normal to the film surface of samples in accordance with the conclusion made by the wide angular X-ray diffraction analysis.[1] However, when the X-ray was introduced from the edge of film samples, namely parallel to the film surface, patterns were obtained that indicated a periodical fluctuation of density in a direction perpendicular to the beam.

Figure 1 illustrates the dependence of the SAXS patterns on compression ratio. Series A shows the SAXS photographs of uncrosslinked samples compressed to different degrees at 150°C (plastically compressed samples). It is recognized arc-like shaped diffractions in meridional direction, characteristic of irregular lamella crystallites structure. With increasing compression ratio, these diffractions become to be diffuse with widening laterally. This is similar to the behavior of polyethylene[8–9] and polypropylene[10–12] when uniaxially stretched at temperatures below the melting point. Series B in the figure shows the SAXS photographs of crosslinked samples compressed to different degrees at 180°C (melt compressed samples). The patterns are different from those of series A. There is observed discrete two-point diffraction in the meridional direction characteristic of ordered lamella crystallite structure. As the compression ratio increases, this two-point diffraction becomes to be clear, shifting to the lower angular range.

On the equator there is recognized the so-called center streak for the both series of samples. In the case of stretched samples such a center streak scattering is usually assumed to be due to rod-like voids[13] or microfibrils[14] in the structure. However, the samples examined here are not thought to be associated with such voids or microfibrils since they are made by uniaxial compression at high temperatures. These center streaks will indicate the existence of the plate-like crystallites structure.[4]

Figures 2 and 3 show the SAXS profile for these two series of samples with different compression ratios; (A) compressed at 150°C in the partially crystalline state (plastically compressed samples) and (B) compressed at 180°C in the melt (melt-compressed samples). In the case of the plastically compressed samples (A), the 2θ angle at the maxima shifts to higher angles and the scattering intensity decreases as the compression ratio increases. Contrary, in the case of the melt-compressed samples the 2θ angle at the maxima shifts to lower angles and the scattering intensity increases with increasing compression ratio.

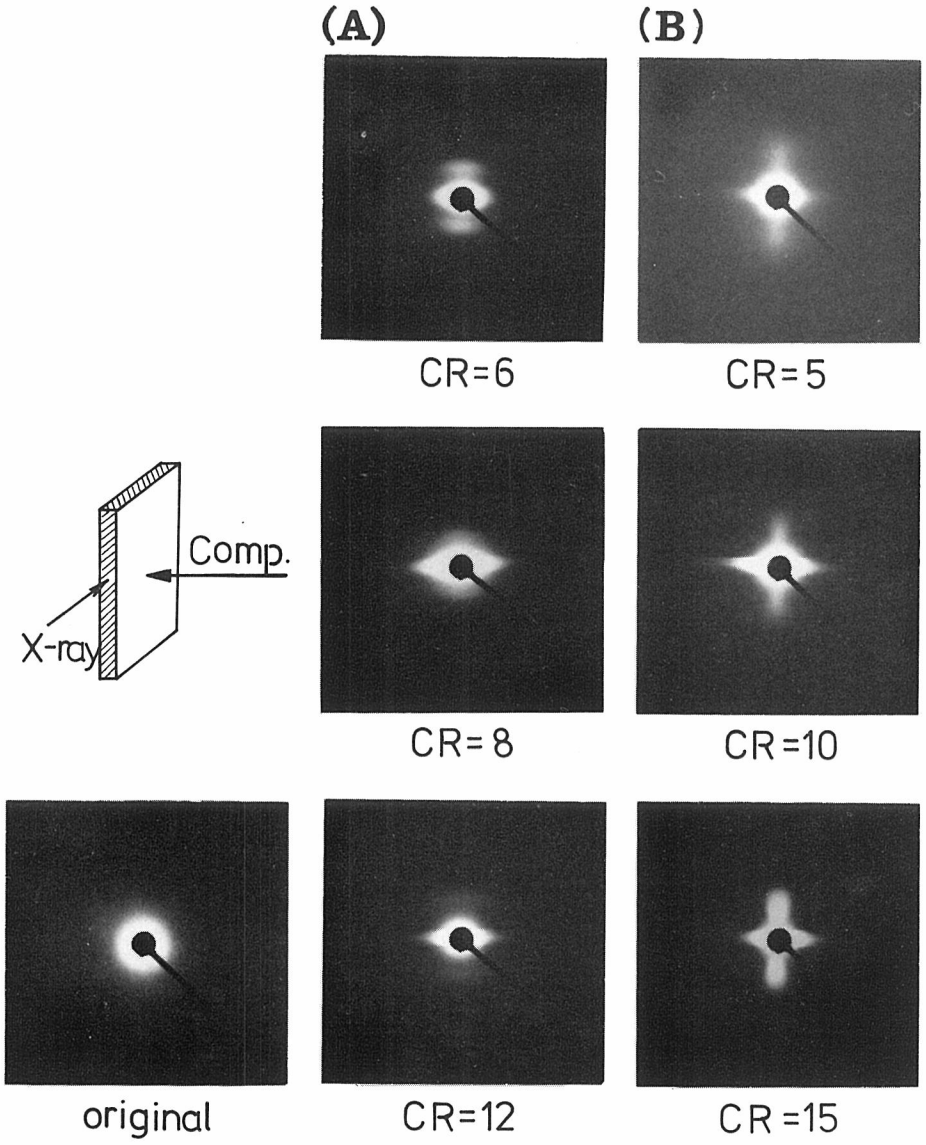

Fig. 1. Small angle X-ray diffraction patterns for polypropylene sample compressed to different degrees at 150°C (Series A) and at 180°C (Series B). Compression ratio is indicated in each pattern.

Consider first the change of the scattering intensity with changing compression ratio. As can be seen in Table 1, the degree of crystallinity slightly increases with increasing degree of compression for the both series of samples. It is usually expected that the scattering intensity is increased with increasing crystallinity. However, the scattering intensity appreciably decreases for the plastically compressed samples but increases for the melt-compressed samples as the crystallinity increases. Peterlin *et al.*[8-9] observed a decrease in the scattering intensity when a polyethylene sample was uniaxially stretched in the partially crystalline state. They attributed this phenomenon to decrease in the density difference between the crystalline and amorphous phases accompanying the plastic stretch-

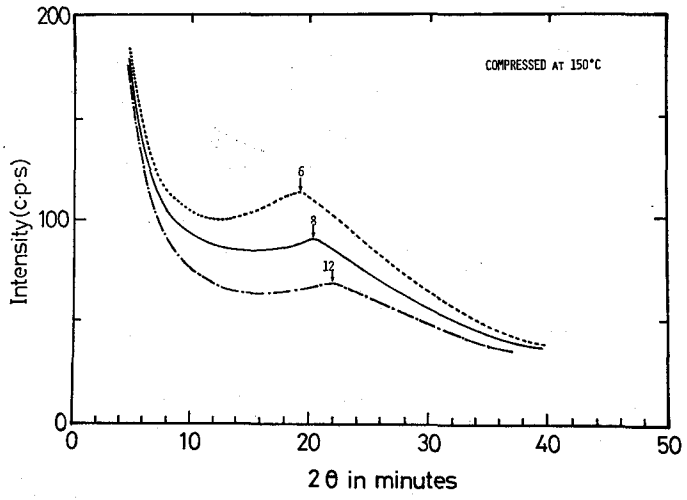

Fig. 2. Angular dependence of SAXS of polypropylene films compressed at 150°C.

ing. They considered that the density of the crystalline phase decreased due to a production of defects while that of the amorphous phase increased accompanying the stretching. The decrease of the scattering intensity observed here for the plastically compressed polypropylene samples may be similar to that as discussed by them. However, when the crosslinked polypropylene is compressed in the melt, the density of the crystalline phase probably does not decrease but slightly increase while that of the amorphous phase is held unchanged in a similar manner to the case that a crosslinked polyethylene is compressed in the melt.[4] Therefore, the density difference between the crystalline and amorphous phases will be increased when the crosslinked polypropylene sample is compressed in the melt. This well explains the enhanced increase of the scattering intensity observed for the melt-compressed samples.

In Figure 4 the long periods evaluated from the SAXS profile are plotted against the

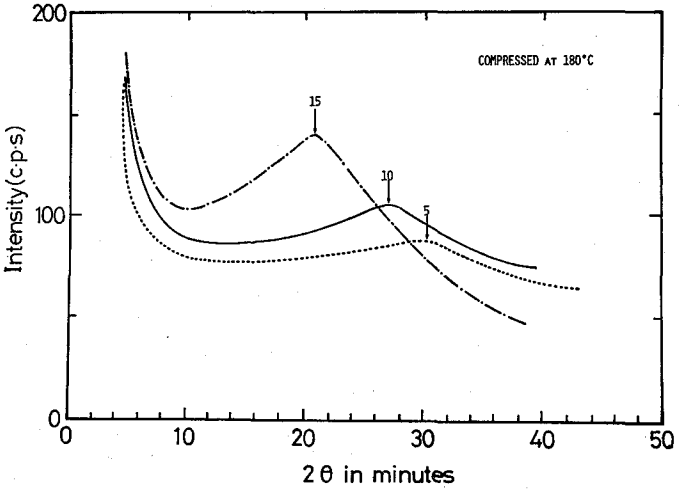

Fig. 3. Angular dependence of SAXS of polypropylene films crystallized from the melt under compression.

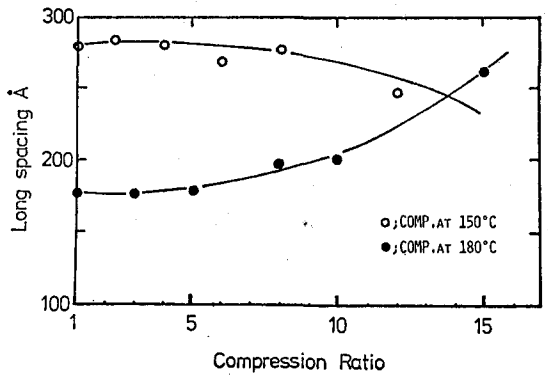

Fig. 4. Variation of the long period as a function of compression ratio for polypropylene films prepared under different conditions.

compression ratio for the two series of samples. It is evident that the long period of the melt-compressed samples increase conspicuously in the direction perpendicular to the compression direction with increasing compression ratio. Contrary, the long period of the plastically compressed samples is decreased with increasing compression ratio. This difference will reflect the difference of the phase structure between the two series of samples in a similar way to the case that crosslinked polyethylene is compressed in the melt or in the partially crystalline state.[4)]

2. Fusion Behavior

The fusion curves obtained by the DSC measurements with a heating rate of 10°C/min for uncrosslinked and crosslinked gel samples compressed at 150°C are shown in Figure 5. By compression, the melting point arises. Note that a small shoulder associated with the major fusion peak is detectable for the compressed samples in a low temperature range. Appearance of similar small shoulder has been recognized by Adams[15)] and Okajima

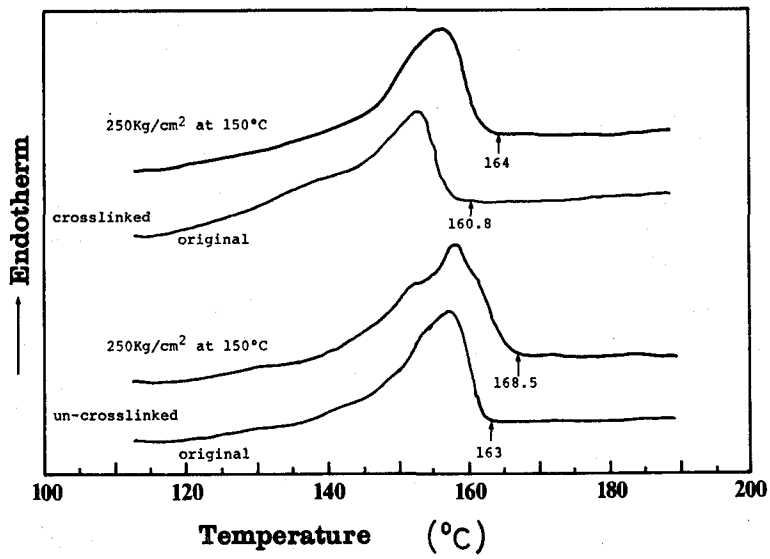

Fig. 5. DSC thermograms for polypropylene films compressed below the melting temperature.

et al.[16] for biaxially stretched polypropylene samples. It should indicate a heterogeneity or dual crystalline structure in samples. But the shoulders recognized are too weak so that no further consideration is allowable.

Figure 6 represents the DSC thermograms for the melt-compressed samples. The shape of the thermograms varies according to the compression ratios. As can be seen, the melt-compressed samples show an endothermic peak with a long "tail", persisting to 173°C. In particular it is to be noted here that for the samples compressed to high degrees weak but clearly distinguishable peaks appear in a higher temperature range of the major fusion peak. Similar dual or multiple fusion curve is sometimes reported for other polymers such as polyethylene,[17–19] polyethylene terephthalate,[20] nylon 66,[21] and polyvinyl alcohol[22] with abnormally high melting temperatures, when such polymers are crystallized under very high pressure or under conditions involving molecular orientation. Also for polypropylene when crystallized from the solution under high degree of stirring or from the melt under uniaxial stretching, very high melting temperature is reported by Monobe *et al.*[23], and Ishikawa *et al.*[24] However, such clear dual peaks recognized in this work have never been reported up to data. This type of thermograms assumes a unique phase structure of the samples, made from the particular mode of crystallization; crystallization from the melt, involving high degree of molecular orientation with aid of crosslinking. The dual fusion curve as well as high melting point are generally characteristic for samples, regardless of polymer sort, which are crystallized under conditions involving molecular orientation. Those should indicate a dual structure or the presence of very highly ordered crystallites with large dimensions.

In Table I, are filed the density and the degree of crystallinity determined from the density measurements, the melting temperature, and the enthalpy of fusion of the compress-

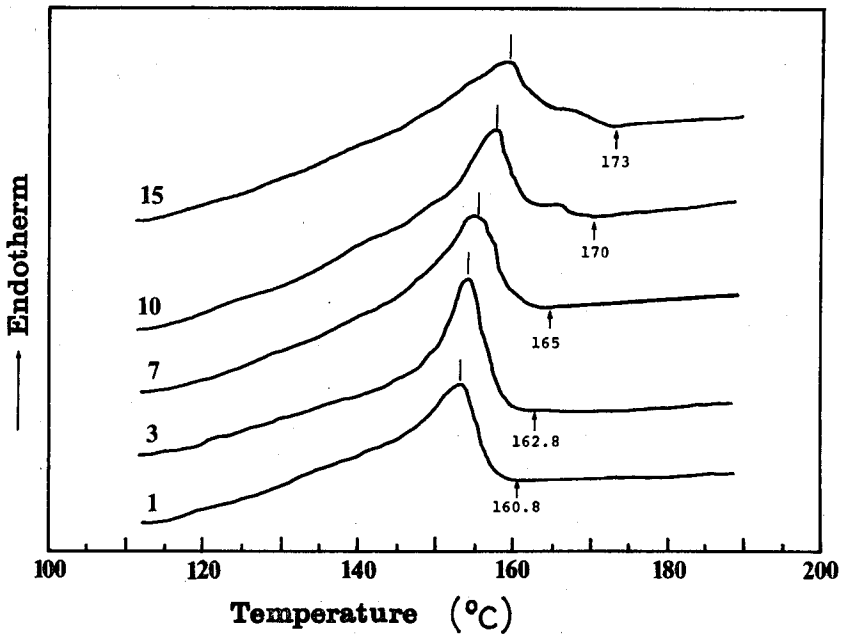

Fig. 6. DSC thermograms for crosslinked polypropylene films made from the melt under compression.

Table I. Density, Melting Point and Heat of Fusion of the Crosslinked Polypropylene Samples of Different Compression Ratio.

Sample	Comp. Ratio	Density g/cm³	Crystallinity $(1-\lambda)_d$	T_m (°C)	ΔH cal/g
Original		0.9045	0.657	163.0	18.6
Gel		0.9042	0.652	160.8	16.6
Non-cross Comp. at 150°C	1	0.905	0.664	163.3	19.2
	6	0.9055	0.672	163.7	19.7
	8	0.906	0.676	164.6	18.5
	12	0.906	0.676	164.0	17.8
Gel sample Comp. at 180°C	1	0.9035	0.645	160.0	13.6
	2	0.904	0.651	162.2	16.2
	3	0.9042	0.652	162.8	15.7
	5	0.9055	0.672	163.0	18.3
	7	0.9050	0.664	162.8	17.4
	9	0.9055	0.672	169.3	19.7
	10	0.906	0.676	170.0	20.7
	15	0.906	0.676	173.0	21.5

ed samples. It is shown that the melting temperature rises and heat of fusion increases, when compressed in the melt, in accordance with increasing compression ratio. But such tendency is hardly recognized for the plastically compressed samples.

3. Effects of Heating Rate in DSC scanning

In determining the melting temperature of a polymer by DSC, one must consider an effect of superheating as well as recrystallization during the scanning. Figure 7 shows the

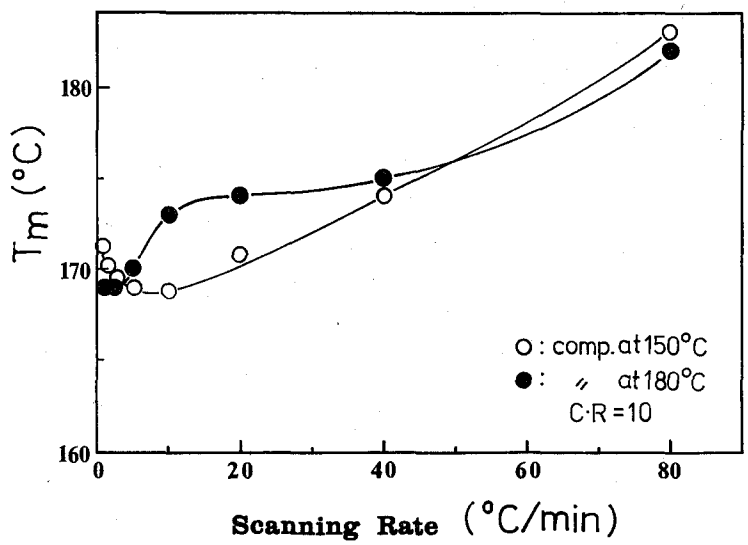

Fig. 7. Melting temperature vs. scanning rate for crosslinked polypropylene crystallized from the melt under compression and polypropylene films compressed below the melting temperature.

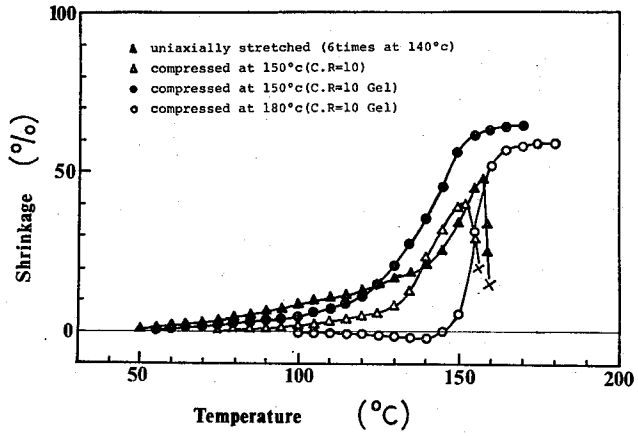

Fig. 8. Thermal shrinkage curves of polypropylene films.

melting point for the two series of samples as a function of heating rate. For the samples compressed at 150°C the curve shows a minimum at a heating rate of 10°C/min. The heightening of Tm at very low heating rate is probably due to an annealing effect, which involves recrystallizations, disappearance of small crystallites and growth to larger ones. As a result, the melting points may rise. On the other hand, for the sample crystallized from the melt under compression, the melting point drastically increases with increasing heating rate; superheating effect is recognized. It is thought that the superheating occurs if the oriented state of the amorphous material with a reduced entropy is maintained during the scan due to the high rate of heating. Fibrillar or extended chain crystals have shown to be particularly susceptible to this phenomenon.[25] In general, the larger size of the

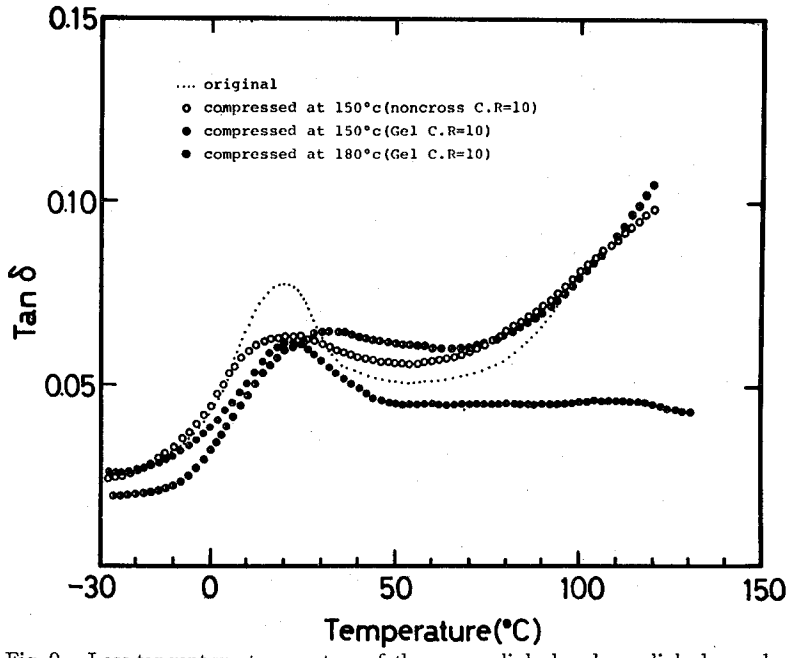

Fig. 9. Loss tangent vs. temperature of the uncrosslinked and crosslinked samples compressed at 150°C and 180°C.

crystallites and the more ordered crystal phase are associated with the greater tendency to this phenomenon. Consequently, this difference may be due to the presence of very stable crystallites in the melt-compression samples.

4. Shrinkage with Heating

The characteristic phase structure and the thermal properties of the oriented samples examined above will be closely related to the macroscopic thermal shrinkage or thermal expansion behavior.

In Figure 8 the shrinkage by heating in air for the films compressed at temperature below or above the melting point is plotted against temperature. Here, we see again a great difference in the thermal shrinkage behavior between the two series of samples. The plastically compressed samples begin to shrink at about 50–70°C and further shrink until the melting point. Contrary, the melt-compressed sample with a compression ratio of 10 does not exhibit appreciable shrinkage up to 145°C, at which the partial fusion is indicated by the DSC scanning, and above 150°C it shrinks very rapidly.

The excellent dimensional stability observed here for the melt-compression samples must be caused by the relaxed state in the amorphous chains.

5. Dynamic Mechanical Properties

The molecular mobility in the amorphous phase of a crystalline polymer is thought

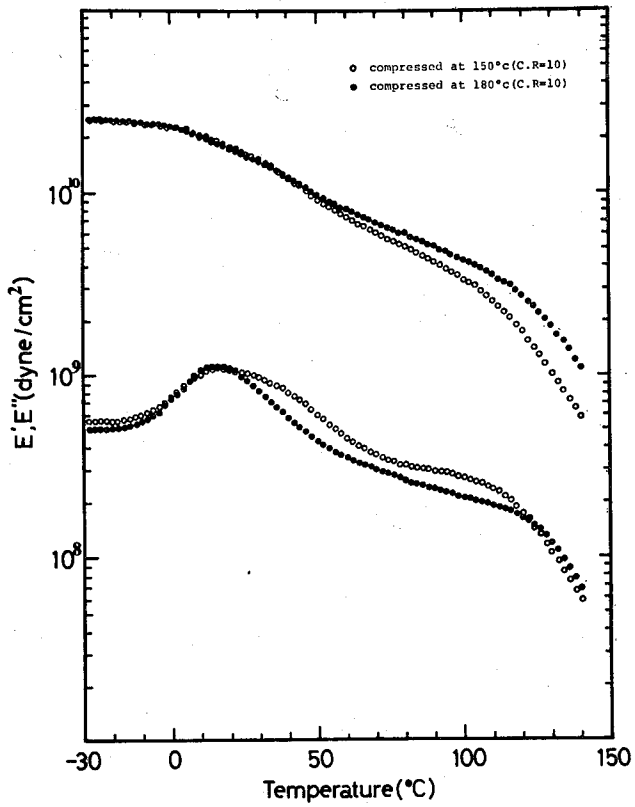

Fig. 10. Temperature dependency of dynamic modulus E′ and dynamic loss E″ for the crosslinked gel samples compressed at 150°C and 180°C.

to depend greatly on the orientation of molecular chains. We study in this section the influence of the compression under various conditions on the viscoelastic behaviors.

In Figures 9 and 10, tan δ and E′, E″ are plotted against temperature for samples compressed at 150°C or 180°C. In the case of th esamples compressed at 150°C, with increasing degree of compression the absorption peak (Ta) in a vicinity of room temperature shifts to a higher temperature and becomes wider and somewhat vague. On the other hand, in the case of the melt-compressed sample, such enhanced elevation of the peak temperature is not recognized and the peak does not widen appreciably, although the value of tan δ becomes small.

The distinct difference in the dynamic viscoelastic behavior recognized here for the two series of samples should reflect the difference in the phase structure of samples. For a cold drawn polypropylene film, Owen and Wyckoff reported a similar behavior to the plastically compressed samples and they attributed the origin to a paracrystalline state of their sample.[26] The T_a transition is generally assigned to a micro-Brownian movement of amorphous molecular chains. Therefore, the higher temperature of T_a of the plastically compressed samples will indicate the stretched state of amorphous molecular chains. On the other hand, the lower temperature of T_a for samples compressed in the melt indicates unstretched and relaxed state of molecular chains in the amorphous phase.

As discussed above, the molecular state of the noncrystalline phase of the compressed samples differs greatly, depending on the mode of compression; compressed in the melt or in the partially crystallized state. We next consider the effect of the degree of compression, when the crosslinked samples are compressed in the melt. In Figure 11 the value of tan δ for the melt-compressed samples with different compression ratios is plotted against temperature. There is observed clear peaks in the vicinity of room temperature for all

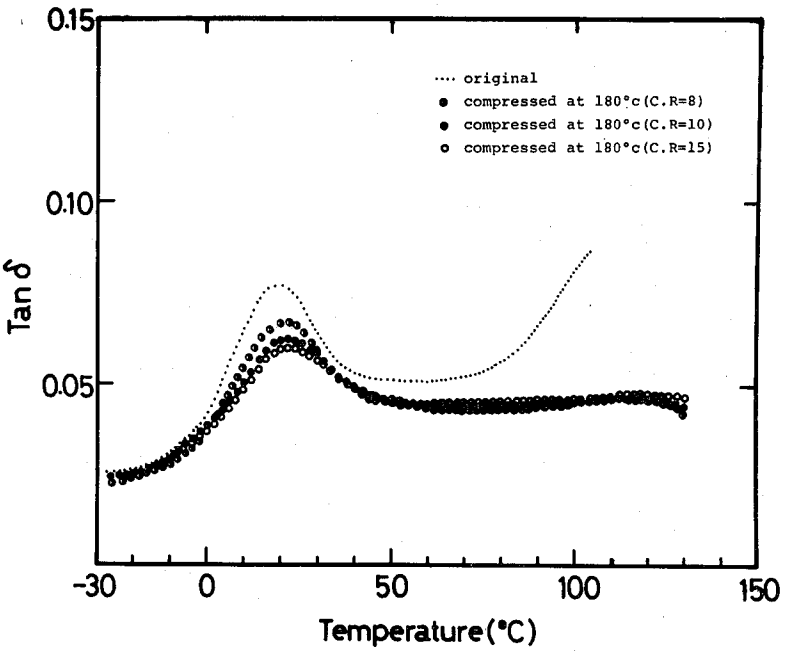

Fig. 11. Loss tangent vs. temperature for the crosslinked gel samples compressed in the melt to different degrees.

samples, corresponding to the α_a transition. The peak area of tan δ decreases appreciably with increasing degree of compression, probably corresponding to minor increase of the degree of crystallinity as expected from the density increase (see Table I). It is to be noted here that the peak temperature T_a is not increased appreciably even if the sample is compressed as highly as to a compression ratio of 15. This indicates that noncrystalline molecular chains are in a rather non-restricted state with a larger segmental motion in the temperature range, almost equivalent to the uncompressed sample, although slight increase of restriction for molecular motion can be suggested by minor shifting of T_a to a high temperature for samples with larger degrees of compression. This is quite contrary to the plastically compressed samples, for which enhanced elevation of T_a is observed at lower degrees of compression, showing that the conformational freedom of noncrystalline molecular chains is strongly restricted due to such a compression as expected.

In Figure 12, the values of E′ and E″ are plotted against temperature. There are again observed clear peaks of E″ in the vicinity of room temperature corresponding to the α_a-transition. This behavior well supports the above-mentioned structural characteristics concerning the noncrystalline material of the samples. Furthermore, the data in the figure give some information of the crystalline phase of the samples. There are observed shoulder-like peaks (α_c) in the E″ plot in the temperature range of 100–140°C. The position of the peak shifts to a high temperature and the intensity thereof increases as the degree

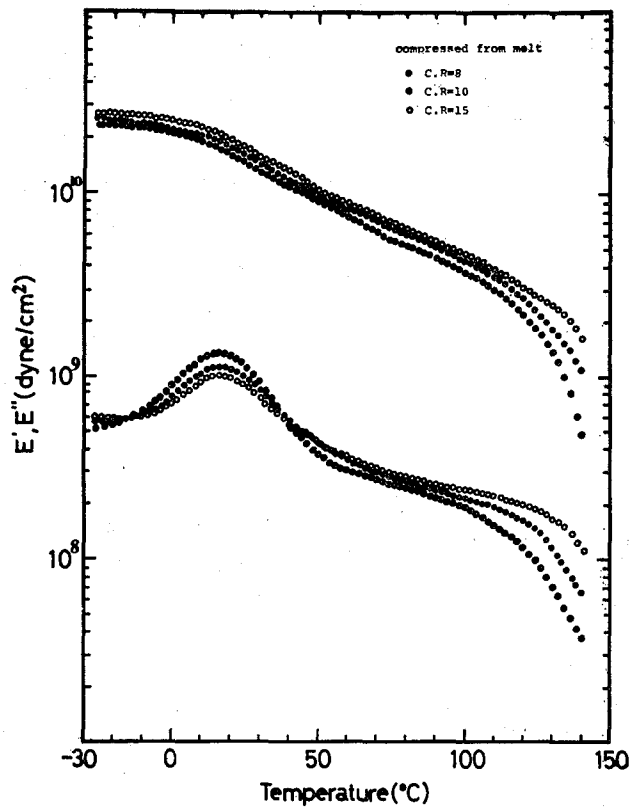

Fig. 12. Temperature dependency of dynamic modulus E′ and dynamic loss E″, for the crosslinked gel samples compressed in the melt to different degrees.

of compression increases. It is also seen that the samples of higher degres of compression is associated with higher values of E′ and pronounced decrease in the value of E′ occurs with increasing temperatures. Since the absorption of this polymer in this temperature range can be assigned as an energy loss in the crystalline phase,[27] these results will lead a conclusion that the degree of crystallinity not only increases but also the crystalline phase in the structure becomes stable and ordered as the degree of compression increases.

IV. SUMMARY

It has evidently been shown that if a lightly crosslinked gel sample is compressed to a high extent in the molten state, the resultant product by subsequent cooling is generally associated with various characteristic structure and properties such as regular lamella crystalline structure and high melting point with excellent dimentional stability for heating. The results of small-angle X-ray scattering, thermal and dynamic mechanical properties show that the phase structure of such melt-compressed samples is quite different from that of the samples that are compressed below the melting point in an usual manner. This characteristic crystalline structure of the product resembles that of lightly crosslinked polyethylene which is crystallized from the molten and compressed state involving molecular orientation.

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